(11) Japanese Patent Publication No. 15138/1985

(24)(44) Publication Date: April 17, 1985

(54) Title of the Invention:

ELECTRIC DOUBLE LAYER CAPACITOR

(21) Japanese Patent Application No. 7768/1979

(22) Filing Date: January 25, 1979

(65) Japanese Patent Laid-Open No. 99714/1980

(43) Laid-Open date: July 30, 1980

(72) Inventors: Atsushi NISHINO

Iwao TAJIMA

Takayoshi MURANAKA;

(71) Applicant: Matsushita Electric Industrial Co., Ltd.

SPECIFICATION

(57) Claims

1. An electric double layer capacitor which utilizes an electric double layer formed in an interface between a polarizable electrode and an electrolyte, characterized by using a carbon fiber as the polarizable electrode.

2. The electric double layer capacitor as set forth in Claim 1, characterized in that an activated carbon fiber which is produced by activating the carbon fiber is used as the polarizable electrode.

3. The electric double layer capacitor as set forth in Claim 2, characterized in that the activated carbon fiber of a raw paper form is used as the polarizable electrode.

4. The electric double layer capacitor as set forth in any one of Claims 1, 2, and 3, characterized in that a phenolic type carbon fiber is used as the polarizable electrode.

Detailed Description of the Invention

The present invention relates to electric double layer capacitors and, when more particularly explained, the present invention is to provide an electric double layer capacitor in which not only processability and application efficiency of a polarizable electrode is improved, but also a charging capacity per unit volume is large by employing a carbon fiber as the polarizable electrode.

Heretofore, as a polarizable electrode of the electric double layer capacitor of this type, used is a thin plate, a net of a metal or a punching metal such as aluminum as it is, or a surface of any one of these current collector metals is roughened by, for example, etching processing and the like to prepare a metallic current collector and, then, on both surfaces of the thus prepared metallic current collector, mold-pressed is the polarizable electrode material comprising activated carbon, or deposited is a rubber-like article by subjecting

it to rolls of rolling processing whereby the polarizable electrode is produced.

However, in the polarizable electrode which has been produced using such a current collector as described above, there exist drawbacks that a contact between the metallic current collector and the activated carbon electrode is not strong and, particularly, in a spiral structure in which the polarizable electrode is allowed to be thin by being subjected to the rolls of the rolling processing and, then, wound, an activated carbon electrode layer outside the current collector and another activated carbon electrode layer inside the current collector are subjected to opposite stresses to each other whereby the contact between the current collector and the activated carbon electrode becomes weaker; for this reason, internal resistance of the electric double layer capacitor is gradually increased, application efficiency of the activated carbon electrode layer is gradually decreased and the like.

Further, in a case of the above-described conventional structure, when the electric double layer capacitors are mass-produced in a large quantity, these problems as described above are even more serious. Namely, due to a peeling-off, drop-off or the like between the current collector and the activated carbon electrode layer which is possibly generated when the polarizable electrode is wound in a spiral form, a variance of a capacity, a decrease of the application efficiency

of the activated carbon electrode layer, and an increase of the internal resistance while in service are generated whereupon a capacity change, a variance of charging time and the like are derived; on this occasion, these are important problems from a standpoint of a commercial value.

In order to solve these drawbacks, the present invention uses a carbon fiber for the polarizable electrode.

Fist of all, the carbon fiber used in the present invention will be described in detail below. It is necessary that the carbon fiber which satisfies an object of the present invention has a large surface area, a small electric resistance, sufficient flexibility and tensile strength required for being processed in a spiral form of a thin piece, and sufficient chemical resistance required for withstanding an electrolyte for a prolonged time.

When the carbon fibers which satisfy such an object as described above are classified, there are 4 types: a phenolic type (cured novolak fiber), a rayon type, an acrylic type, and a pitch type. Further, a method of changing these raw material fibers into the carbon fibers or the activated carbon fibers is shown in a figure.

As is appreciated from this figure, there are two methods: a method in which the raw material fiber is directly carbonize-activated; the other method in which the raw material fiber is once changed into the carbon fiber and, then, activated.

Ordinarily, the raw material fiber is once changed to the carbon fiber and, then, activated at a temperature of from 700°C to 800°C under an atmosphere of a mixed gas comprising a steam and a nitrogen gas. Further, ordinarily, since the surface area, and the electric resistance and the flexibility are in an inverse proportional relation among them, as the carbon fiber is activated into the activated carbon fiber, the surface area becomes larger, the carbonization yield is decreased and the electric resistance and the flexibility become deteriorated. For being used as the polarizable electrode of the electric double layer capacitor, the carbonization yield is preferably from 10% to 80%, though depending on types of the raw material fibers; when the carbonization yield is less than 10%, though the surface area becomes larger, some types of the raw material fibers lose the flexibility thereby becoming difficult to withstand mechanical strength at the time of being wound in a spiral form or being subjected to current collector electrode processing; further, when the carbonization yield is more than 80%, though the electric resistance, the flexibility, carbon fiber strength and the like are excellent, the surface area becomes smaller and an electric capacity per unit volume becomes smaller; hence, such a case as described above is not preferable. As herein used, the carbonization yield of the fiber is expressed by:

weight of carbon fiber/weight of raw material fiber x 100(%); or

weight of activated carbon fiber/weight of raw material fiber x 100(%),

wherein, as an example in a case of a phenolic fiber, the carbonization yield of the carbon fiber is from 50% to 58% and the carbonization yield of the activated carbon fiber is from about 18% to about 55%.

Characteristics of carbon fibers of different types are shown in Table 1.

Table 1

		Phenolic type	Rayon type	Acrylic type	Pitch type	Coconut husk charcoal
Surface area (m^2/g)		1500-2000	1400	900	700	800
Tensile strength (Kg/mm^2)		50-70	5-10	200-250	60	-
Modulus (Kg/mm^2)		2000-3000	1000-2000	2000-3000	3000-3500	-
Specific resistivity ($\times 10^{-5}$ Ω-cm)		1000-3000	2000-3000	800-1000	2000-3000	-
Electrode shapes	Felt/Mat forms	Yes	Yes	Yes	Yes	No
	Cloth form (plain/twilled fabrics)	Yes	No	No	No	No
	Paper form	Yes	Yes	No	No	Yes
Primal characteristics of carbon fiber as inert electrode		Strong; excellent in flexibility; optimum as electrode	Hard; brittle to some extent	Hard; brittle to some extent; but superior to coconut husk charcoal	Hard; brittle; but superior to coconut husk charcoal	Thin type electrode necessitating current collector; extremely small capacity efficiency

As is apparent from Table 1, the acrylic and pitch types lack the flexibility to some extent as a whole and the surface areas thereof are small to some extent. As for the rayon type, though the surface area is large, the fiber itself is brittle; the carbon fiber thereof in a felt form is popular; though it is certainly difficult to make raw paper therefrom, it is possible to prepare it in a paper form; further, there exists a problem in chemical resistance and water resistance. On the other hand, as for the phenolic type carbon fiber, which is derived from the cured novolak fiber, since the cured novolak fiber is infusible and small in heat shrinkage, it is not necessary for this phenolic type carbon fiber to preliminarily change the raw material fiber thereof into an infusible state; further, it is possible to activate-carbonize a textile or a non-woven fabric thereof as it is; furthermore, it is strong and excellent in flexibility; hence, it is particularly excellent as being the polarizable electrode of the electric double layer capacitor. Still furthermore, there are a multiple of characteristics in making paper from the phenolic type carbon fiber as a raw material; it is particularly recognized that raw paper made by using a specified Kynol (trade name of a phenolic type fiber, available from Nippon Kynol Inc.) as a binder has characteristics of being excellent in a plurality of aspects such as flexibility, electric resistance, chemical resistance,

winding processing strength, processing accuracy, electric capacity, cost and the like.

Next, embodiments according to the present invention will be described in detail with reference to a conventional example.

In the first place, as a conventional example, a punching metal (t=0.1 mm) of aluminum which has been subjected to etching processing was used as a current collector and, then, both surfaces of the thus prepared current collector were each processed with an activated carbon electrode layer, derived from coconut husk charcoal powders as raw materials, having a thickness of 200 μ by rolling processing and, thereafter, the resultant article was cut in a shape having electrode sizes (20 cm x 2.5 cm x 500 μ) to obtain an electrode. The thus obtained electrode was provided with a lead made of aluminum by a known method and, then, a separator made of polypropylene was interposed between two pieces of such electrodes as thus obtained above and wound as a whole by a winder in a spiral form. Subsequently, the thus wound article was put in a case made of aluminum having sizes of a diameter of 16 mm and a length of 33 mm and, after being provided with a groove, the case was provided with a cover and filled with an electrolyte (by a vacuum impregnation method) and, thereafter, an opening thereof was crimp-sealed to prepare the conventional example.

Next, embodiments according to the present invention are described. A rayon type activated carbon fiber in a felt form,

an acrylic type activated carbon fiber in a felt form, a pitch type activated carbon fiber in a felt form, a phenolic type activated carbon fiber in a felt form, a phenolic type activated carbon fiber in a cloth form, and a phenolic type activated carbon fiber in a paper form were used as respective activated carbon fiber raw materials. These raw materials were each cut in a shape (20 cm x 2.5 cm x 0.5 mm) of a polarizable electrode and, then, a separator of a PTFE type was interposed between 2 pieces of each of the thus prepared polarizable electrodes of the activated carbon fiber and wound as a whole by a winder in a spiral form. On this occasion, a winding operation was executed while an opposite electrode was arranged such that only one end surface thereof had a step of about 1 mm. While using an aluminum lead wire for leading each of the electrodes out, a current collector terminal and a lead terminal of each of the electrodes were simultaneously formed on each end surface thereof by a plasma spraying method using aluminum powders. The thus formed electrodes comprising the activated carbon fibers were subjected to assembling and housing operations in a same manner as in the conventional example and, on this occasion, an electrolytic liquid of a 1 M/l propylene carbonate solution of tetraethylammonium perchlorate was used as an electrolyte.

Characteristics of the thus prepared examples according to the present invention and the conventional example were compared and the results are shown in Table 2.

As is apparent from Table 2, the examples according to the present invention in which the activated carbon fibers were used as the polarizable electrodes can remarkably be improved in the capacity per unit volume and the internal resistance.

Table 2

		Electrode layer thickness mm^2	Apparent electrode volume cm^3	Capacity per unit volume F/cm^3
Conventional example (Coconut husk charcoal)		0.5	2.5	41
Examples according to the present invention	Rayon type in felt form	0.5	2.5	190
	Acrylic type in felt form	0.5	2.5	265
	Pitch type in felt form	0.5	2.5	415
	Phenolic type in felt form	0.5	2.5	520
	Phenolic type in cloth form	0.5	2.5	695
	Phenolic type in paper form	0.5	2.5	765

Further, in order to compare the characteristics in cases in which the carbon fibers and the activated carbon fibers that had been obtained by activating the foregoing carbon fibers were used, using various phenolic type carbon fibers each in a felt form differentiated only in carbonization ratios from

each other as carbon fiber raw materials, polarizable electrodes were prepared in a same manner as in the above-described embodiment which used the activated carbon fibers and, further, using the thus prepared polarizable electrodes, finished articles each as an electric double layer capacitor weSre prepared to compare characteristics thereof. Results are shown in Table 3. As is appreciated from Table 3, even in a state of carbon fibers, the capacity per unit volume and the internal resistance can remarkably be improved in a same manner as in the above-described activated carbon fibers.

Table 3

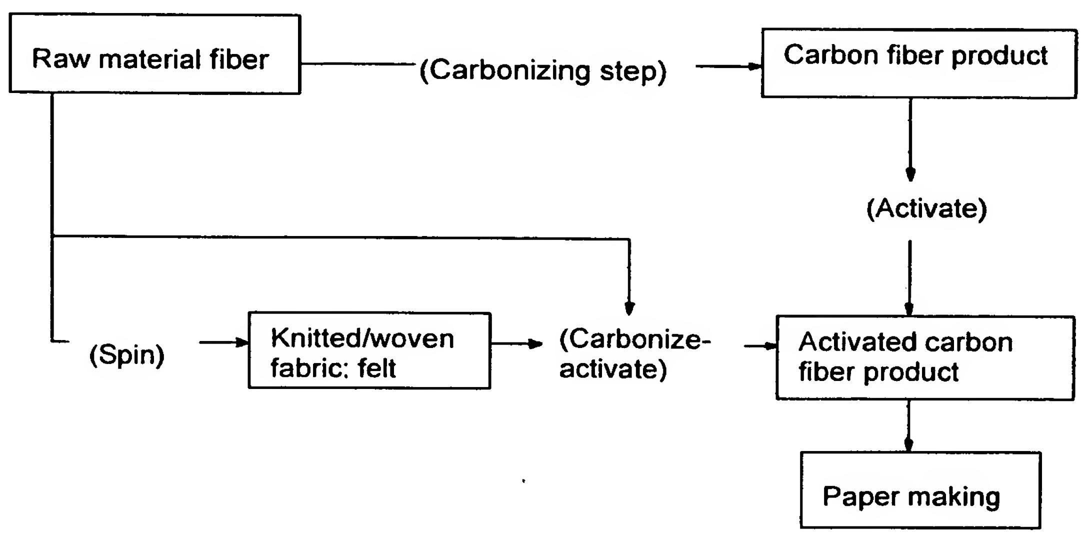
	Carbonizing yield	Capacity per unit volume F/cm^3	Internal resistance
Phenolic type carbon fiber	90	20	0.015
"	60	240	0.05
"	30	475	0.11
"	10	520	0.14

As described above in detail, the electric double layer capacitor according to the present invention not only can improve the capacity per unit volume and the internal resistance, but also can attempt to achieve a quality stabilization, a yield

rate improvement, and a cost reduction; hence, an industrial value thereof is extremely large.

Brief Description of a Drawing

The figure is a diagram for explaining a method of changing into a carbon fiber or an activated carbon fiber which is used in an electric double layer capacitor according to the present invention.



⑲日本国特許庁（JP）　⑪特許出願公告

⑫特許公報（B2）　昭60－15138

⑤Int.Cl.⁴　識別記号　庁内整理番号　㉔㊹公告　昭和60年(1985) 4月17日
H 01 G 9/00　A－7924－5E

発明の数 1 （全4頁）

㊿発明の名称　電気二重層キヤパシター

㉑特　願　昭54－7768　㊺公　開　昭55－99714
㉒出　願　昭54(1979) 1月25日　㊸昭55(1980) 7月30日

⑫発明者　西野　敦　門真市大字門真1006番地　松下電器産業株式会社内
⑫発明者　田島　厳　門真市大字門真1006番地　松下電器産業株式会社内
⑫発明者　村中　孝義　門真市大字門真1006番地　松下電器産業株式会社内
⑪出願人　松下電器産業株式会社　門真市大字門真1006番地
⑭代理人　弁理士　中尾　敏男　外1名
審査官　則澤　孝次

1　　2

㊼特許請求の範囲

1　分極性電極と電解質界面で形成される電気二重層を利用した電気二重層キヤパシターにおいて、分極性電極として炭素繊維を用いたことを特徴とする電気二重層キヤパシクー。

2　分極性電極として、炭素繊維を賦活した活性炭繊維を用いたことを特徴とする特許請求の範囲第1項に記載の電気二重層キヤパシター。

3　分極性電極として、抄紙状の活性炭繊維を用いたことを特徴とする特許請求の範囲第2項に記載の電気二重層キヤパシター。

4　分極性電極として、フエノール系炭素繊維を用いたことを特徴とする特許請求の範囲第1項、第2項または第3項記載の電気二重層キヤパシター。

発明の詳細な説明

本発明は電気二重層キヤパシターに関するもので、更に詳細に説明すれば、分極性電極として炭素繊維を用いることにより、分極性電極の加工性、利用効率を改善するとともに、単位体積当りの充電容量の大きい電気二重層キヤパシターを提供するものである。

従来、この種の電気二重層キヤパシターの分極性電極としては、アルミニウムのような金属の薄板、ネツトまたはパンチングメタルをそのまま用いるか、若しくはこれらの集電体金属表面をエツチング処理などにより表面を粗面化したものを金属集電体として、この両表面に、活性炭からなる分極性電極材料を成型プレスするか、またはゴム状のものを圧延ロールにかけて担持させることにより分極性電極を製造していた。

しかしながら、このような集電体を用いて製造した分極性電極は金属集電体と活性炭電極との接触が強固でなく、特に圧延ローラにかけて薄くした分極性電極を巻回して渦巻き構造にしたものは、集電体の外側の活性炭電極層と集電体の内側の活性炭電極層とは応力がそれぞれ逆にかかるため、集電体と活性炭電極との接触は一層弱くなり、このため電気二重層キヤパシターの内部抵抗が次第に増大したり、活性炭電極層の利用効率が次第に低下する等の欠点があつた。

また前述の従来の構造の場合、電気二重層キヤパシターを大量に量産するときに、これらの問題は更に深刻である。すなわち、分極性電極を渦巻状に巻回するときに生じる集電体と活性炭電極層との剝離、脱落等による容量のバラツキや活性炭電極層の利用効率の低下や使用時に内部抵抗が増大し、容量変化や充電時間のバラツキ等が生じ、商品価値上重要な問題となつている。

本発明ではこれらの欠点を解決するために、分極性電極に炭素繊維を用いたものである。

先ず、本発明で用いる炭素繊維について詳述すると、本発明の目的にかなう炭素繊維は、表面積が大きく、電気抵抗が小さく、薄片状の渦巻形状

の加工に必要な柔軟性と引張強度と長期間の電解質に耐える耐薬品性とを有さねばならない。

このような目的にかなう炭素繊維を類別すると、フエノール系（硬化ノボラツク繊維）、レーヨン系、アクリル系、ピツチ系の四種類がある。また、これらの原料繊維を用いて、炭素繊維化あるいは活性炭繊維する方法を示すと図のようになる。

この図から理解できるように、原料繊維を直接炭化、賦活する方法と、一旦炭素繊維化したあとい賦活する方法とがある。一般的には、一度炭素繊維化した後、水蒸気と窒素からなる混合ガス雰囲気下で700～800℃の温度で賦活化を行なう。また、一般に、炭素繊維の表面積と電気抵抗、柔軟性とは反比例の関係にあるので、炭素繊維から活性炭繊維に賦活するに従つて表面積の増大がともない、炭化収率は低下し、電気抵抗、柔軟性は悪くなる。電気二重層キヤパシターの分極性電極として用いるためには、原料繊維の種類によつて異なるが、炭化収率は10～80%程度が好ましく、炭化収率が10%以下では表面積は大になるが、原料繊維によつて柔軟性がなくなり、渦巻状に巻回したり、集電極加工時の機械的強度に耐えられなくなる。また、逆に炭化収率80%以上では、電気抵抗、柔軟性、炭素繊維強度等は優れているが、表面積が小となり単位体積当りの電気容量が小となるので好ましくない。ここで、繊維の炭化収率とは、

$$\frac{\text{炭素繊維の重量}}{\text{原料繊維の重量}} \times 100\ (\%)\ \text{または}$$

$$\frac{\text{活性炭繊維の重量}}{\text{原料繊維の重量}} \times 100\ (\%)$$

で表わされるものを炭化収率といい、フエノール繊維を例にとると、炭素繊維の炭化収率は50%～58%で、活性炭繊維の炭化収率は18～55%程度となる。

表1にそれぞれ種類の異なる炭素繊維の特長を示している。

表　1

		フエノール系	レーヨン系	アクリル系	ピツチ系	ヤシガラ粒状炭
表面積（m²/g）		1500～2000	1400	900	700	800
引張強度（Kg/mm²）		50～70	5～10	200～250	60	－
引張弾性率（Kg/mm²）		2000～3000	1000～2000	2000～3000	3000～3500	－
電気比抵抗（$\times 10^{-5}\Omega$-cm）		1000～3000	2000～3000	800～1000	2000～3000	－
電極形状	フエルト状・マツト状	有	有	有	有	無
	クロス状（平織・綾織）	有	無	無	無	無
	ペーパー状	有	有	無	無	有
不活性電極としての炭素繊維の主な特徴		強くて柔軟性に優れ、電極として最適	硬くて稍々もろい	硬くて稍々もろいが、ヤシガラ炭より優れる	硬くてもろいが、ヤシガラ炭より優れている	薄状の電極にするには集電体が必要で充電効率が極めて小である

この表1より明らかなように、アクリル系、ピツチ系は、一般に稍々柔軟性にかけ、また表面積が稍々小ない。また、レーヨン系は表面積が大であるが、繊維がもろく、またフエルト状の炭素繊維は普及しているが、抄紙化が困難で、ペーパー状は可能であり、耐薬品性、耐水性に問題がある。一方、フエノール系炭素繊維は硬化ノボラツク繊維を原料とするもので、このフエノール系炭素繊維は硬化ノボラツク繊維が不溶融性で且つ熱収縮が小さいために原料繊維を予め不融化する必要がなく、織物や不織布がそのまま活性炭化ができ、また強くて柔軟性に優れているので、電気二重層キヤパシターの分極性電極として、特に優れている。また、フエノール系炭素繊維を原料にした抄紙化には数々の特長を有し、特にフエノール系炭素繊維を原料にバインダーとして特殊カイノール（日本カイノール株式会社製フエノール系繊維の商品名）を用いて抄紙化したものは、柔軟

性、電気抵抗、耐薬品性、巻回加工強度、加工精度、電気容量、コスト等の数々の面で極めて優れた特長を有することが認められた。

次に、従来例を参考に、本発明の具体的実施例を詳述する。

先ず従来例として、粉末ヤシガラ炭を原料にアルミニウムのパンチングメタル（t＝0.1㎜）のエツチング処理を施したものを集電体とし、この集電体の両面に厚み200μの活性炭電極層を圧延により加工処理し、電極寸法（20㎝×2.5㎝×500μ）の形状に切断して電極を得た。これに公知の方法で、アルミニウムのリードを取付け、そして2枚の電極間にポリプロピレンのセパレーターを挟み込み、巻き取り機で、渦巻状に巻き取る。そして、これを直径16㎜φ、長さ33㎜のアルミニウムのケースに入れ、ケース溝入れ、蓋のとりつけ、電解液の注入（真空含浸）、かしめ封口を行なうことにより従来品を得た。

次に、本発明品について述べると、レーヨン系フエルト状活性炭繊維、アクリル系フエルト状活性炭繊維、ピツチ系フエルト状活性炭繊維、フエノール系フエルト状活性炭繊維、フエノール系クロス状活性炭繊維、フエノール系抄紙状活性炭繊維からなるそれぞれの活性炭繊維原料を用い、これを分極性電極形状（20㎝×2.5㎝×0.5㎜）に切断し、それぞれの活性炭繊維の電極間にPTFE系のセパレーターを挟み込み、巻き取り機で渦巻状に巻き取る。この時、対極の端面のみ1㎜程度の段差を設けて巻き取る。電極の取り出しはアルミニウム導線を用い、アルミニウム粉末を用いたプラズマ溶射法により、両端面から両極の集電とリード端子とを同時に形成する。このようにして得られた活性炭繊維からなる電極を前述の従来品と同様な方法で、組立、ハウジングを行ない、そして電解液としては、プロピレンカーボネートを溶媒として、1M／ℓのテトラエチルアンモニウムパークロレートを電解質としたものを用いた。

このようにして製作した本発明品と従来品との特性を表2に比較して示している。

この表2から判るように、分極性電極として活性炭繊維を用いた本発明によれば、単位体積当りの容量、内部抵抗を著しく改善することができる。

表　2

		電極層の厚さ㎜	見掛け電極体積㎤	単位体積当りの容量F／㎤
従来例（ヤシガラ炭）		0.5	2.5	41
本発明品	レーヨン系フエルト状	0.5	2.5	190
	アクリル系フエルト状	0.5	2.5	265
	ピツチ系フエルト状	0.5	2.5	415
	フエノール系フエルト状	0.5	2.5	520
	フエノール系クロス状	0.5	2.5	695
	フエノール系ペーパー状	0.5	2.5	765

また、炭素繊維とこれを賦活することにより得られる活性炭繊維とを用いた場合における特性を比較するために、フエノール系フエルト状炭素繊維をそれぞれ炭化収率のみを変化させた炭素繊維原料として用い、そして前述した活性炭繊維を用いた実施例と同様な方法で分極性電極とし、さらに電気二重層キヤパシターとしての完成品とした場合の特性を調べた。この結果を表3に示しており、この表3から判るように炭素繊維の状態であつても、前述の活性炭繊維と同様に単位体積当りの容量、内部抵抗を著しく改善することができる。

表　3

	炭化収率	単位体積当りの容量F／㎤	内部抵抗
フエノール系炭素繊維	90	20	0.015
〃	60	240	0.05
〃	30	475	0.11
〃	10	520	0.14

以上のように本発明の電気二重層キヤパシターによれば、単位体積当りの容量、内部抵抗を著し

く改善することができるだけでなく、品質の安定化、歩留改善、価格低減を図ることができ、その工業的価値は極めて大なるものである。

図面の簡単な説明

図は本発明の電気二重層キャパシターで用いる炭素繊維化または活性炭繊維化する方法を説明するための図である。